

A Review on Decomposition of Hydrazine and Its Kinetics as a Novel Approach for CO-Free H₂ Production

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Abstract

Mechanism and kinetics of hydrazine decomposition as hydrogen rich material were studied in details. Several mechanisms were studied and compared. Temperature sensitivity of reaction and probability production of different products (nitrogen, hydrogen and ammonia) according to their behaviours on catalyst surfaces were investigated. Also kinetics of hydrazine decomposition on iridium surface was maintained, analyzed and compared with common surfaces. It was investigated that different surfaces influence on mechanism of reaction and the concentration change of produced materials.

Keywords

Hydrazine; Catalytic Decomposition; Mechanism; Kinetics

Introduction

Nowadays, hydrogen production with lesser amounts of impurity is important in many processes. Hydrazine is a substance which is hydrogen-rich and with high energy content. Its hydrogen percentage is as high as 12.5 wt.%. Hydrazine is very attractive as a hydrogen source for proton exchange membrane fuel cell (PEM), particularly when the fuel cells are operated under special conditions such as in unmanned space vehicles or satellites where the energy is very limited (Zheng et al., 2005; Lee et al., 2005; Song et al., 2010; Ghanbari Pakdehi et al., 2013).

The reaction of hydrazine was emphasized in many researches (Zheng et al., 2005; Konnov and Ruyck, 2001; Smlth and Solomon, 1982; Wood et al., 1975; Schmidt, 2001). This reaction is exothermic and does not need any energy to be provided from outside (Zheng et al., 2005). Decomposition of hydrazine can be performed by two methods: Catalytic decomposition (on metal surfaces and supported metal particles (Lee et al., 2005; Konnov and Ruyck, 2001)) and thermal decomposition (Zheng et al., 2005; Konnov and Ruyck, 2001). Hydrazine products after complete decomposition are N₂ and H₂. In hydrazine

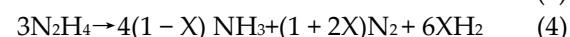
decomposition reaction, NH₃ is not only the product but also the intermediate (Li et al., 2005). The products are also CO-free since no carbon atoms are present in hydrazine (Zheng et al., 2005).

The main objectives of this work are: (a) to study the catalytic decomposition of hydrazine and its mechanisms; (b) to study the kinetics of hydrazine decomposition.

Catalytic Decomposition of Hydrazine

Hydrazine can be decomposed over catalysts at room temperature. The decomposition is an exothermic reaction and does not need any energy to be provided from outside (Zheng et al., 2005). An important aspect of the catalytic decomposition of hydrazine process is that hydrazine decomposition usually does not follow the fixed chemical stoichiometry. It could be affected by catalysts, temperature and pressure (Zheng et al., 2005; Ghanbari Pakdehi et al., 2013; Wood et al., 1975).

Four possible hydrazine catalytic decomposition pathways are shown in Eqs. (1) to (4) (Zheng et al., 2005; Song et al., 2010; Larsen et al., 2001). Reactions 1, 2, and 3 have all been catalyzed by various metal-based catalysts, the most effective being those with incomplete d shells.



$$X = \frac{2(\text{H}_2)}{2(\text{H}_2) + 3(\text{NH}_3)} \times 100\% \quad (5)$$

Hydrazine decomposition can be described as following reactions (1) and (2). The produced ammonia decomposes further into hydrogen and nitrogen according to reaction (2) at high temperatures (>300°C). The overall reaction can be expressed as Eq.

(3). The H_2 selectivity of the catalyst, X , is taken as the decomposition percentage and is calculated from the amounts of hydrogen and ammonia (Eq. (4)). Generally, the H_2 selectivity of a catalyst is equal to the percent of decomposition of the intermediate ammonia at high temperatures. Hence, the H_2 selectivity of catalyst, X is also used to evaluate the extent of ammonia decomposition according to reaction (5) (Zheng et al. 2005).

The heterogeneous reactions involved in the mechanism support an accumulation of N_2H_4 in the initial period of the reaction (at low contact times), which explains the delayed formation of the final products and the occurrence of the induction period and thus confirming the degenerated, homogeneous-heterogeneous branched chain mechanism for NH_3 thermal decomposition (Konnov and Ruyck, 2001).

Mechanisms of Hydrazine Decomposition

Zhang et al. (Zhang et al., 2009) maintained the general set of reaction mechanisms involved in the decomposition of hydrazine. As they referenced, a researcher used mass spectroscopy to study the kinetics behind the shock wave of hydrazine diluted in argon over a temperature range of 1200-2500°C and determined the overall rate constant within this temperature range. Konnov and Ruyck (Konnov and Ruyck, 2001) developed a detailed N/H reaction mechanism, consisting of 51 reactions for 11 species. This mechanism was validated by comparing kinetic modelling results with measurements of hydrazine pyrolysis in shock waves and in hydrazine decomposition flames at low and atmospheric pressures. The overall calculated rate of decomposition by this mechanism agrees well with experiments for pure hydrazine and its mixtures with argon, nitrogen, water, and ammonia.

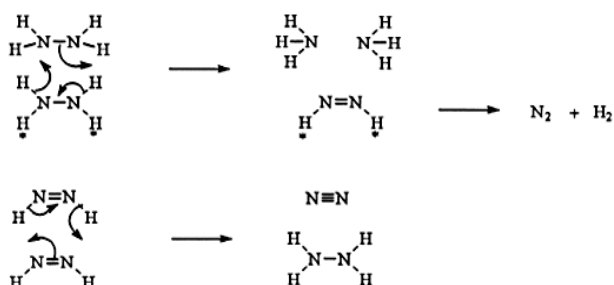
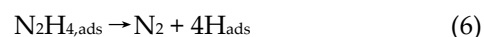


FIG. 1 SAYERS MECHANISM FOR CATALYTIC HYDRAZINE DECOMPOSITION (Larsen et al., 2001).

Larsen (Larsen et al., 2001) mentioned a mechanism for hydrazine decomposition in his paper. He proposed that an adsorbed hydrazine transfers two

hydrogens to another hydrazine to cleave the N-N bond and form two molecules of ammonia and an adsorbed cis diazine (HN_2NH , also known as diimide). The diazine then disproportionates to give N and hydrazine or decomposes to N and H. The diazine disproportionation is well established and is a significant complication in the use of diazine to reduce double bonds. This mechanism is outlined in Fig. 1.

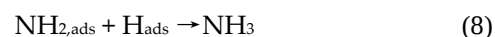
Hydrazine decomposition mechanism seems to break down into distinct low- and high-temperature parts. As suggested by some researchers, direct decomposition reaction on the surface, generates N_2 that desorbs without association with the surface (Lee et al., 2005):



The nearly identical desorption feature for NH_3 at low temperatures suggests that the N_2 and NH_3 production mechanisms are coupled. Lee et al. (Lee et al., 2005) suggested that NH_3 dissociatively can be adsorb on the catalyst, at least above 573°C. They concluded that the NH_3 is produced in such a way that at least some fraction does not become bound to catalyst surface, and desorbs promptly. Also Li et al. (Li et al., 2005) indicated that several NH_3 production mechanisms are possible, depending on how hydrazine is bound on catalyst at low temperature. If substantial $N_2H_{4,ads}$ is present, then NH_3 might be generated in reaction with H_{ads} from the N_2 generation reaction:



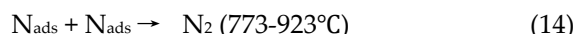
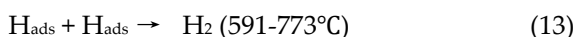
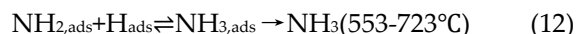
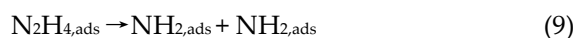
Alternatively, if N_2H_4 is dissociatively adsorbed at low temperatures, then NH_3 could be generated by reaction with surface radical species, such as NH_2 :



In either case, the reaction could occur by H diffusion from neighbouring sites on the catalyst surface, but also could occur via a concerted mechanism in a complex, as has been suggested by Lee et al. (Lee et al., 2005). If H_2 also is desorbed at low temperature, it would presumably have to form by recombination of H_{ads} . Even if some low-temperature H_2 desorption occurs, it is clear that a substantial fraction of the hydrogen remains on the surface to be desorbed as H_2 and NH_3 at high temperatures.

In addition to the low-temperature mechanism, all three products are also observed to desorb in broad, overlapping features in the temperature range from 553 to 923°C. On the basis of the similarities of these desorption features to those observed following dissociative adsorption of NH_3 on various catalyst

surfaces, the high-temperature features are attributed to recombination of N_xH_y species left on the surface by hydrazine decomposition. Such a mechanism can be written in different ways, but a reasonable set of reactions is (Li et al., 2005):



Consistent with this sequential mechanism is the observation that, once the temperature is high enough to drive recombinative desorption of H_2 , the associated reduction in H_{ads} concentration rapidly shuts down NH_3 production.

Prasad and Gland(Prasad and Gland, 1991) studied hydrazine decomposition on a clean rhodium surface. They reported that absorbed imide (NH) is as a stable intermediate during hydrazine and ammonia decomposition on Ni, Rh, Ir, W, and Mo surface. This suggests that N_2H_4 is dissociatively adsorbed on Rh surface at $493^\circ C$ giving adsorbed imide, nitrogen atoms, and hydrogen atoms. It was proposed that a portion of the NH_{ads} may recombine to form diimide (N_2H_2), which is desorbed from the Rh surface above $473^\circ C$. The yield of diimide increases with increasing initial hydrazine coverage as expected for a recombination process.

Diimide formation has been confirmed chemically by observing the diimide yield in the presence of co-adsorbed hydrogen and co-adsorbed oxygen during hydrazine decomposition on Rh. In the presence of co-adsorbed hydrogen, the yield of diimide increased substantially for both N_2H_4 and NH_3 . In the presence of hydrogen, the decomposition of NH_{ads} should be inhibited, thus increasing the diimide yield.

TABLE 1 SUGGESTED MECHANISM OF HYDRAZINE DECOMPOSITION ON RHODIUM SURFACE(Prasad and Gland, 1991)

Step description	Mechanism
Direct decomposition	$N_2H_4 \rightarrow (220\text{ K}) \rightarrow N_2(\text{gas}) + H_{ads} \quad (15)$
	$N_2H_4 + H_{ads} \rightarrow (220\text{ K}) \rightarrow N_2H_2(\text{gas}) + H_{ads} \quad (16)$
Dissociative adsorption	$N_2H_4 \rightarrow (220\text{ K}) \rightarrow N_2H_2(\text{gas}) + H_{ads} \quad (17)$
Dissociation of surface intermediates	$NH_{ads} \rightarrow (460\text{ K}) \rightarrow N_{ads} + H_2(\text{gas}) \quad (18)$
Hydrogenation	$NH_{ads} + H_{2,ads} \rightarrow (220-360\text{ K}) \rightarrow NH_3(\text{gas}) \quad (19)$
Recombination	$NH_{ads} + NH_{ads} \rightarrow (\text{above } 220\text{ K}) \rightarrow N_2H_2(\text{gas}) \quad (20)$
	$N_{ads} + N_{ads} \rightarrow (635\text{ K}) \rightarrow N_2(\text{gas}) \quad (21)$
	$H_{ads} + H_{ads} \rightarrow (360\text{ K}) \rightarrow H_2(\text{gas}) \quad (22)$

The suggested mechanism of hydrazine decomposition on rhodium surface is listed in Table 1.

These researches indicate that the mechanism of hydrazine decomposition in various catalysts is very complicated. It is obvious that temperature influences on mechanisms and their progresses. Production of different intermediate components in catalyst surface can lead to produce products. Chemically, it decomposes with an exothermic reaction into ammonia and nitrogen when composed to a catalyst bed. Unfortunately, if the reaction is allowed to continue, the ammonia decomposes in an endothermic reaction. It is obvious that changing in either the reaction mechanism or the fraction of catalyst surface available for reaction takes place in the temperature range $723-773^\circ C$.

Kinetics Studies

The catalytic decomposition of hydrazine on iridium surfaces has been of interest in recent years (Lee et al., 2005; Konnov and Ruyck, 2001; Makled and Belal, 2009). Hydrazine decomposes on iridium based catalyst almost exclusively to form N_2 and NH_3 whereas H_2 is also the products over Rh, Pt and Pd catalysts between $60^\circ C$ and $160^\circ C$. Another interesting aspect of catalytic decomposition of hydrazine is that greatly different between the general commercial noble metal catalyst (exhibiting the suitable catalytic activity for hydrazine decomposition) and iridium based catalysts. Generally, the most efficient catalyst contains about 36 wt.% metallic iridium dispersed on an alumina support (Li et al., 2005).

Smith and Solomon (Smith and Solomon, 1982) investigated the kinetics of hydrazine decomposition over iridium surface. In the acquisition of kinetic data from heterogeneous systems, it is important to select conditions for which the effects of reactant and/or product transport to and from the catalytic surface can be accounted for quantitatively. The measured reaction rate per unit area (R) is given by (Smith and Solomon, 1982):

$$R = k(T) \prod_i^{n_i} c_{s_i} = k_m (c_g - c_s) \quad (23)$$

Where $k(T)$ is the rate coefficient for the reaction, c_{s_i} is the concentration of species i at the catalyst surface, n_i is the reaction order with respect to species i , and c_g and c_s represent the concentration of hydrazine in the bulk and at the catalyst surface, respectively. The mass transport coefficient, k_m is given by:

$$k_m = 1.82 \frac{G}{\rho} Sc^{-2/3} Re^{-0.51} \quad (Re < 350) \quad (24)$$

G is the mass velocity based on the superficial cross-

sectional area of the reactor, ρ is density, Sc is the Schmidt number and Re is the Reynolds number based on the effective diameter of the catalyst particle. The concentration of hydrazine at the catalyst surface is given by:

$$\frac{c_s}{c_g} = 1 - \frac{R}{R_d} \quad (25)$$

Where R is reaction rate and R_d is the diffusion controlled rate, $R_d = kmc_g$. Thus, if the reaction orders with respect to products are negligibly small, we have:

$$R = k(T)c_s^n = k(T) \left[c_g \left(1 - \frac{R}{R_d} \right) \right]^n \quad (26)$$

Some experiments indicated that hydrazine decomposition followed rate Eq. (26) according to model that was introduced in Eq. (27):

$$R = 6.81 \times 10^8 \exp \left[-\frac{2939 \pm 1079}{T} \right] c_s^{1.41 \pm 0.44} \quad (27)$$

The surface reaction rate for hydrazine (R) is in units of $\text{g.mol.s}^{-1}.\text{cm}^{-2}$. The hydrazine surface concentration (c_s) has units of g.mol.cm^{-3} . Error limits are for 95% confidence levels.

The best correlation over a reactant surface concentration range of 7×10^{-10} $\text{g.mol.s}^{-1}.\text{cm}^{-2}$ to 1×10^{-9} $\text{g.mol.s}^{-1}.\text{cm}^{-2}$ as obtained with an order with respect to hydrazine of 1.41 ± 0.44 .

It was illustrated that the apparent activation energy of the specific surface reaction rate was found to be 5.84 ± 2.14 kcal. g.mol^{-1} over a temperature range of 733 to 973°C. Below 733 °C, the rate exhibits much stronger temperature dependence. At 703°C, the observed rate was an order of magnitude lower than that predicted on the basis of the higher temperature data. For temperatures smaller than 703°C, the rate was below the detection limits of the apparatus. A discontinuous change in temperature dependence, such as that observed between 733 and 703°C, is usually indicative of either a change in the reaction mechanism or of the nature of the catalytic surface.

Sackheim et al. (Sackheim et al., 1980) suggested other reaction rates for catalytic (heterogeneous) decomposition of hydrazine:

$$R_{\text{N}_2\text{H}_4} = 1 \times 10^{10} e^{-\left(\frac{2777.78}{T}\right)} c_{\text{N}_2\text{H}_4} = k_1 c_{\text{N}_2\text{H}_4} \quad (28)$$

For ammonia catalytic decomposition:

$$R_{\text{NH}_3} = 1 \times 10^{14} e^{-\left(\frac{2777.78}{T}\right)} \frac{c_{\text{NH}_3}}{c_{\text{H}_2}^{1.6}} = k_2 \frac{c_{\text{NH}_3}}{c_{\text{H}_2}^{1.6}} \quad (29)$$

Some catalysts such as Co/SiO_2 , Rh/SiO_2 and Ir/SiO_2 clearly did not produce much H_2 at low temperatures (<300°C). The reaction paths over them are mainly reaction Eq. (1) to form ammonia and nitrogen. When the reaction temperature increases to 300°C and higher,

the produced ammonia disassociates further into hydrogen and nitrogen (Zheng et al., 2005).

It is found that Ni, Pd and Pt metals over various supports all catalyzed hydrazine decomposition with a high H_2 selectivity at low temperatures (Zheng et al., 2005). N_2H_4 decomposed over Ni catalyst into H_2 and N_2 with more than 90% selectivity at 30–40°C. The preparation method and the support of the nickel catalysts played important roles in the catalytic activity and H_2 selectivity. These findings suggested that Ir and Ni catalyst might be a good candidate for catalytic decomposition of hydrazine at rather mild temperatures for producing CO-free H_2 for PEM fuel cells. In addition, it was found that all catalysts of group VIII metals were efficient for hydrazine decomposition and able to produce H_2 at high temperatures (>350°C). Especially, over Ru, Co, Rh, and Ir catalysts, hydrazine decomposed readily into H_2 and N_2 at high temperatures. Theoretically, production of H_2 can also be done by hydrazine decomposition over these catalysts under auto thermal conditions. It is obvious that CO-free H_2 can be produced if hydrazine decomposes at high enough temperatures over these catalysts. Calculations have shown that the temperature of the decomposition products can be 604°C when liquid hydrazine decomposes into H_2 and N_2 under adiabatic conditions. Hence, the production of CO-free H_2 by catalytic decomposition of hydrazine under auto thermal conditions is highly feasible. One of the best commercial catalysts for hydrazine decomposition is the iridium on gamma-alumina (20–40 wt%) catalyst (Lee et al., 2005; Neto et al., 2011; Vieira et al., 2005).

There is a popular understanding in catalysis that only a suitable interaction between the catalyst and the reactants can yield a high catalytic activity, while too strong or too weak interaction would yield a low activity. As the heat of formation of the respective metal nitride decreases from the left to the right of the periodic table, the strength of the metal–N interaction on the surface of the catalyst decreases as well (Zheng et al., 2005). On the other hand, the metal–H interaction also decreases almost linearly as the d band orbital of the metal becomes more occupied. Hence, the trends of catalytic activity and selectivity in hydrazine decomposition over catalysts might be related to the regular variation of chemisorption energy of hydrogen and nitrogen on the metals.

Conclusion

Hydrazine decomposition was studied for producing

CO-free H₂ for PEM fuel cells. It was found that several mechanisms can describe the behavior of hydrazine decomposition on surface catalysts. The amounts of absorbed and resorbed species on catalysts surface can influence the concentration profile of products.

It was found that some catalysts catalyzed hydrazine decomposition with a high H₂ selectivity at low temperatures. The type of catalyst and the operation temperature controlled the decomposition rate and production selectivity of hydrazine. In addition, it was revealed that all catalysts of group VIII metals were efficient for hydrazine decomposition. Kinetics studies showed that rate of reaction in catalytic decomposition is complicated and can be influenced by parameters such as temperature and concentration of species.

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